

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

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Serial No. Application of 09/890,326

Filed: January 31, 2000

For: SURFACE-PROTECTED TRANSPARENT PLASTIC COMPOSITE MATERIAL

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Hon. Commissioner of Patents and Trademarks  
Washington, D.C. 20231

D E C L A R A T I O N

I, Tatsuya EKINAKA, am one of inventors of U.S. Patent Application, Serial No. 09/890,326 and am fully familiar with the content of the invention. I have read Office Action issued on January 8, 2004 in the examination of the above U.S. Patent Application.

For studying differences between the invention of Nakayama reference (JP 59-109528) cited by the Examiner and the invention of the present application (U.S. Patent Application, Serial No. 09/890,326), I have conducted the following experiments.

The "present application" stands for U.S. Patent Application, Serial No. 09/890,326 hereinafter.

I. Summary of Experiments

I-(1) Experiment A:

A polycarbonate (PC) resin composite material was prepared by substantially duplicating Example 4 of the present specification.

That is, in Experiment A, a first layer coating solution (I-4) described in Table 5 of the present specification was used as a first layer coating solution, and a second layer

coating solution (II-4) described in Table 6 of the present specification was used as a second layer coating solution.

The above second layer coating solution (II-4) was a solution containing an organosiloxane from the following components (a), (b) and (c).

(a) 100 parts of a water-dispersible colloidal silica (S-30),

(b) 151.1 parts of methyltrimethoxysilane (MTMOS),

(c) 33.3 parts of tetraethoxysilane hydrolysis condensate solution (Y).

#### I-(2) Experiment B:

In the second layer coating solution in Experiment A, half (50 % by weight) of methyltrimethoxysilane (MTMOS) as component (b) was replaced with ethyltrimethoxysilane, to prepare a second layer coating solution in Experiment B. A PC resin composite material was prepared in the same manner as in Experiment A except that the second layer coating solution in Experiment A was replaced with the above-prepared second layer coating solution.

## II. Experiments

In the following Experiments A and B, the following synthesis and preparation numbers represent numbers described in the present specification, page 43, line 14 to page 52, line 17.

- (i) Synthesis of acrylic resin (AC-4)  
Referential Example 4
- (ii) Preparation of acrylic resin solution (h-4)  
Referential Example 22
- (iii) Preparation of organosiloxane resin solution (i-2)  
Referential Example 41
- (iv) Preparation of Melamine resin formulation (j-3)  
Referential Example 47

- (v) Preparation of first layer coating solution (I-4)  
Referential Example 52
- (vi) Preparation of second layer coating solution (II-4)  
Referential Example 75
- (vii) Preparation of PC resin composite material  
Example 4

#### II-(1) Experiment A

##### (i) Synthesis of acrylic resin (AC-4)

A flask having a reflux condenser and a stirrer and having nitrogen substituted for air inside were charged with 74 parts of methyl methacrylate (to be abbreviated as "MMA" hereinafter), 15 parts of 2-(2'-hydroxy-5'-methacryloxyethylphenyl)benzotriazole (to be abbreviated as "MEBT" hereinafter), 11 parts of 2-hydroxyethyl methacrylate (to be abbreviated as "HEMA" hereinafter), 0.16 part of azobisisobutyronitrile and 200 parts of 1,2-dimethoxyethane, and these contents were mixed and dissolved. Then, the mixture was allowed to react under nitrogen current at 70°C for 6 hours. The resultant reaction mixture was added to n-hexane for re-precipitation and purification, to give 88 parts of an acrylic copolymer resin (to be abbreviated as "AC-4" hereinafter) having an MMA/MEBT/HEMA composition ratio of 74/15/11 by weight ratio (81.7/14.5/3.8 by molar ratio).

##### (ii) Preparation of acrylic resin solution (h-4)

13 Parts of the above acrylic copolymer resin (AC-4) was dissolved in 16.3 parts of 2-butanone, 27 parts of 4-methyl-2-pentanone, 11 parts of 2-butanol and 9.6 parts of 2-ethoxyethanol, to obtain 63.9 parts of an acrylic resin solution (h-4).

##### (iii) Preparation of organosiloxane resin solutions (i-2)

100 Parts of the methyltrimethoxysilane hydrolysis condensate solution (X), 0.5 part of sodium acetate as a curing

catalyst were mixed to give an organosiloxane resin solution (i-2).

(iv) Preparation of Melamine resin formulations (j-3)

100 Parts of Cymel 300 (hexamethoxymethylated melamine resin supplied by Mitsui-Cytec) and 3 parts of p-toluenesulfonic acid as a curing catalyst were mixed to give a melamine resin formulation (j-3).

(v) Preparation of first layer coating solution (I-4)

76.9 Parts of the acrylic resin solution (h-4), 20 parts of the siloxane resin solution (i-2), 1.1 parts of the melamine resin formulation (j-3) and 2 parts of 2-(2'-hydroxy-5'-t-octylphenyl)benzotriazole (to be referred to as "UV-1" hereinafter) were mixed and dissolved to give 100 parts of a first layer coating solution (I-4).

(vi) Preparation of second layer coating solution (II-4)

10 Parts of 0.05 mol/l hydrochloric acid and 11.1 parts of acetic acid were added to 100 parts of a water-dispersible colloidal silica dispersion (Snowtex 30 (to be abbreviated as "S-30" hereinafter), supplied by Nissan Chemical Industries, Ltd., solid content 30 % by weight), and the mixture was stirred. 151.1 Parts of methyltrimethoxysilane was added to the resultant dispersion with cooling in an ice water bath. The mixture was stirred at 25°C for 1 hour, and 33.3 parts of the tetraethoxysilane hydrolysis condensate solution (Y) and 2.2 parts of potassium acetate as a curing catalyst were mixed with the reaction mixture at room temperature. The mixture was diluted with 188.9 parts of isopropanol to give 496.6 parts of a second layer coating solution (II-4). The coating solution had a pH of 5.4.

(vii) Preparation of PC resin composite material (A)

A dip coating vessel having the form of a rectangular parallelepiped was filled with the first layer coating solution

(I-4), and a 0.5 mm thick transparent sheet made of a PC resin was pre-dipped in the coating solution, lifted up at a constant rate and left at 25° C for 30 minutes, followed by thermal curing at 120° C for 40 minutes. The first layer had a thickness of 3.5  $\mu\text{m}$ . Then, the second layer coating solution (II-4) was applied onto the coating surface of the sheet in the same manner as in the formation of the first layer, and the applied coating solution was left at 25° C for 20 minutes and then thermally cured at 110° C for 2 hours. The second layer had a thickness of 4.0  $\mu\text{m}$ . Table I shows results of evaluation of the resultant PC resin composite material A.

#### II-(2) Experiment B

##### (i) Preparation of first layer coating solution

In Experiment B, the same first layer coating solution (I-4) as that in the above Experiment A was used as a first layer coating solution.

##### (ii) Preparation of second layer coating solution(B)

10 Parts of 0.05 mol/l hydrochloric acid and 11.1 parts of acetic acid were added to 100 parts of a water-dispersible colloidal silica dispersion (S-30), and the mixture was stirred. To the resultant dispersion was added 75.5 parts of methyltrimethoxysilane and 75.5 parts of ethyltrimethoxysilane with cooling in an ice water bath. The mixture was stirred at 25° C for 1 hour, and 33.3 parts of the tetraethoxysilane hydrolysis condensate solution (Y) and 2.2 part of potassium acetate as a curing catalyst were added to the resultant reaction mixture at room temperature. The mixture was diluted with 188.9 parts of isopropanol to give 496.6 parts of a second layer coating solution (B). The coating solution had a pH of 5.4.

##### (iii) Preparation of PC resin composite material (B)

A dip coating vessel having the form of a rectangular parallelepiped was filled with the first layer coating solution

(I-4), and a 0.5 mm thick transparent sheet made of a PC resin was pre-dipped in the coating solution, lifted up at a constant rate and left at 25° C for 30 minutes, followed by thermal curing at 120° C for 40 minutes. The first layer had a thickness of 3.5  $\mu$ m. Then, the second layer coating solution (B) was applied onto the coating surface of the sheet in the same manner as in the formation of the first layer, and the applied coating solution was left at 25° C for 20 minutes and then thermally cured at 110° C for 2 hours. The second layer had a thickness of 4.0  $\mu$ m. Table I shows results of evaluation of the resultant PC resin composite material B.

### III. Evaluations of PC resin composite materials and results

The PC resin composite materials obtained in the above Experiments A and B were evaluated according to methods described in the present specification. That is, the composite materials were evaluated according to the methods described in the present specification, page 42, line 6 to page 43, line 4, with regard to (1) evaluation of appearance, (2) adhesion, (3) abrasion resistance, (4) durability against boiling water (boiling water immersion test) and (5) weatherability.

The following Table I shows the results.

Table I-(1)

Second layer Composition	Weight ratio		
	Colloidal silica	Triaalkoxysilane	Tetraalkoxysilane
		(as $\text{CH}_3\text{SiO}_{3/2}$ )	(as $\text{C}_2\text{H}_5\text{SiO}_{3/2}$ )
(II-4)	27	67	6
B	27	32	35
			6

Table I-(2)

	First layer coating solution	Thickness of first layer ( $\mu\text{m}$ )	Second layer coating solution	Thickness of second layer ( $\mu\text{m}$ )	Appearance	Initial haze	Abrasion resistance
Ex.A	(I-4)	3.5	(II-4)	4.0	Excellent	0.1	1.8
Ex.B	(I-4)	3.5	(B)	4.0	Excellent	0.1	8.5

Table I-(3)

	Adhesion		Boiling water immersion test		Weatherability test			
	First time	Third time	Appearance	Adhesion	Appearance	Adhesion	Adhesion	$\Delta\text{VI}$
				First time	Third time	First time	Third time	
Ex.A	100	100	Excellent	100	100	Excellent	100	0.3
Ex.B	100	100	Excellent	100	100	Excellent	100	0.5

#### IV. Observations of evaluation results

The following can be understood from the results shown in Table 1. The composite material obtained in Experiment A will be referred to as "composite material A", and the composite material obtained in Experiment B will be referred to as "composite material B".

(1) In Experiments A and B, first layers having the same compositions and having the same thickness (3.5  $\mu\text{m}$ ) were formed on 0.5 mm thick transparent sheet made of the same PC resin. Therefore, in the composite materials A and B, the transparent plastic substrates (PC sheets) and the first layers stacked thereon are completely identical.

(2) The composite materials A and B are slightly different from each other in composition of second layer. That is, the second layer formed in the composite material A and the second layer formed in the composite material B are constituted of components (a), (b) and (c) as shown in Table I.

	<u>Composite material A</u>	<u>Composite material B</u>
Component (a)	Colloidal silica 27 %	Colloidal silica 27 %
Component (b)	Methyltrimethoxysilane 67 %	Methyltrimethoxysilane 32 % Ethyltrimethoxysilane 35 %
Component (c)	Tetraethoxysilane 6 %	Tetraethoxysilane 6 %

That is, it can be said that the second layer in the composite material B has a composition in which 50 % by weight of the component (b) (methyltrimethoxysilane) for the second layer in the composite material A is replaced with ethyltrimethoxysilane.

(3) As far as the evaluation results are concerned, the composite materials A and B show no difference in appearance, initial haze, adhesion and boiling water immersion test results. Further, the composite materials A and B show no difference in



appearance and adhesion in the weatherability test.

(4) However, it has been found that the composite material B has a high yellowing index ( $\Delta YI$  value) in terms of weatherability as compared with the composite material A and undergoes slightly yellowing.

(5) Further, the composite material A shows a difference  $\Delta H$  by 1.8 and is remarkably excellent in abrasion resistance. In contrast, the composite material B shows a sharp difference  $\Delta H$  by 8.5. The difference  $\Delta H$  by 8.5 concerning the abrasion resistance means that the surface of the composite material B is scratched in the Taber abrasion test to have an increased haze (%), that is, it means that the transparency of the composite material B is lost.

(6) It can be seen that, for attaining an excellent value in abrasion resistance, it is a very important factor that the component (b) for the second layer should be methyltrimethoxysilane.

(7) As the composite material B shows, the abrasion resistance greatly decreases when 50 % by weight of the component (b) for the second layer is replaced with ethyltrimethoxysilane. It can be therefore said that the content of the methyltrialkoxysilane such as methyltrimethoxysilane as the component (b) for the second layer in the entire trialkoxysilane is required to be at least 70 % by weight for obtaining a composite material having excellent properties (particularly, excellent abrasion resistance).

The undersigned declarant further declares that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application

or any patent issuing thereon.

The 28<sup>th</sup> day of July, 2004

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